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XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON MUCOPHENOXYCHLORIC ACID.

By Harris Eastman Sawyer.

Presented by H. B. Hill, February 14, 1894.

It was found some years ago, by Hill and O. R. Jackson,* that mucobromic acid was decomposed by treatment with baric hydrate, and that the course of the reaction varied, according as the solution was made strongly or feebly alkaline. In the first case, formic, dibromacrylic, and brompropiolic acids were formed. The product in the latter case, as has been shown in a more recent investigation,† was mucoxybromic acid. Hill and Stevens, pursuing the subject further, studied the action of potassic phenylate on mucobromic acid, and obtained a mucophenoxybromic acid whose constitution was established by its conversion into phenoxybromacrylic and phenoxybrommaleic acids.‡ They made, however, no attempt to prepare the corresponding series of chlorine compounds, because of the difficulties then attendant on the preparation of mucochloric acid. As it has become possible to obtain this acid in any desired quantity, it has seemed desirable to continue this work, which is now of more interest because of the relationship between the substituted mucobromic and mucochloric acids, and the recently described crotonolactones of Hill and Cornelison.§

The author would here express his deep obligations to Professor H. B. Hill, at whose suggestion the research was undertaken; and to Mr. Howard Nash, for assistance in some of the analytical work.

Mucophenoxychloric Acid.

The following method has been found most advantageous for the preparation of this acid. A solution of 17.6 grams of potassic hydrate and of 25 grams of crystallized phenol in 25 c. c. of water is cooled to 10°, and 13.2 grams of powdered mucochloric acid stirred in, as rapidly as is possible without rise of temperature. After standing for half or three quarters of an hour, at ordinary temperatures, the potassium salt of the new acid separates as a finely crystalline precipitate, which, after a second strong cooling, is filtered off and washed with a little ice-cold water.

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* These Proceedings, Vol. XVI. p. 188.

† These Proceedings, Vol. XXII. p. 316.

‡ These Proceedings, Vol. XIX. p. 262.

§ These Proceedings, *ante*, p. 42.

From a solution of this salt, hydrochloric acid precipitates mucophenoxychloric acid as an oil, which solidifies on standing, and may be recrystallized from benzol. From a solution of the pure potassium salt, however, the acid is precipitated at once, in the crystalline condition.

I. 0.1750 gram substance gave 0.3412 gram CO_2 and 0.0517 gram H_2O.
II. 0.2602 gram substance gave 0.1652 gram AgCl.
III. 0.3102 gram substance gave 0.1966 gram AgCl.

	Calculated for $C_4H_2(OC_6H_5)ClO_3$.	Found. I.	II.	III.
Carbon	52.98	53.17		
Hydrogen	3.09	3.28		
Chlorine	15.67		15.70	15.68

Mucophenoxychloric acid is sparingly soluble even in warm water, still less in cold. On the spontaneous evaporation of its aqueous solution, it crystallizes out in clusters of long, thin plates, melting at 91°. It is readily soluble in alcohol, ether, chloroform, and benzol, even in the cold, and is extremely soluble in hot benzol. It is dissolved but sparingly by carbonic disulphide and ligroin.

Potassic Mucophenoxychlorate, $KC_4H(OC_6H_5)ClO_3 . H_2O$.

An aqueous solution of the crude potassium salt, saturated at 50°, is filtered while warm, and cooled sharply in a freezing mixture. After some minutes, the salt separates in small rhombic plates which contain one molecule of crystal water. Thoroughly dried by pressure, these suffer no material loss of weight on exposure to the air; over sulphuric acid there is a diminution in weight corresponding to about one fifth of the molecule of water; at 95°, after a further loss approximately equivalent to the remainder of the molecule, browning and slight decomposition set in, making the exact determination of the crystal water impossible.

I. 0.3778 gram air-dried salt gave 0.1166 gram K_2SO_4.
II. 0.6117 gram air-dried salt gave 0.1878 gram K_2SO_4.
III. 0.3891 gram air-dried salt gave 0.1188 gram K_2SO_4.

	Calculated for $KC_4H(OC_6H_5)ClO_3 . H_2O$.	Found.		
		I.	II.	III
Potassium	13.84	13.89	13.79	13.71

Baric Mucophenoxychlorate, $Ba[C_4H(OC_6H_5)ClO_3]_2$.

It was first attempted to prepare this salt by neutralizing a cold aqueous solution of the acid with baric carbonate, and after filtration allowing it to evaporate *in vacuo* over sulphuric acid. This method, which gave satisfactory results with mucophenoxybromic acid,* proved fruitless here, for the solution rapidly became acid, and deposited crystals which, from their form and melting point, 91°, were evidently the free acid. The salt was finally prepared by precipitation of an aqueous solution of the pure potash salt, saturated at 50°, with a similarly saturated solution of baric chloride; on chilling in a freezing mixture, a crystalline precipitate appeared, which was sucked off, and washed with small quantities of ice-cold water, until the washings gave no precipitate with argentic nitrate. The salt crystallizes in small anhydrous rhombic plates, which are extremely soluble, even in the coldest water; and as its solution is so readily decomposed, no attempt was made to recrystallize it for analysis. When pressed dry between filter papers, it remained unchanged in the air, lost only a trifling amount of weight over sulphuric acid, and but a trifle more at 105°.

I. 0.2982 gram substance gave 0.1161 gram $BaSO_4$.
II. 0.2152 gram substance gave 0.0858 gram $BaSO_4$.

	Calculated for $Ba[C_4H(OC_6H_5)ClO_3]_2$.	Found.	
		I.	II.
Barium	23.35	23.60	23.47

No detailed study has yet been made of the decomposition mentioned above; it has, however, been noticed that there is no formation of baric bromide, and that phenol and baric oxalate are set free.

Argentic Mucophenoxychlorate, $AgC_4H(OC_6H_5)ClO_3$.

This salt is best prepared by adding a solution of the potassium salt to an excess of moderately dilute argentic nitrate solution. There is an immediate precipitate of white granular crystals, which is increased in quantity by sharp cooling, and scratching. The salt is sparingly soluble in water, more readily in warm than cold, and is deposited by the warm concentrated solution in short compact prisms, which contain no crystal water.

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* These Proceedings, Vol. XIX. p. 264.

0.4115 gram substance gave 0.1771 gram AgCl.

	Calculated for $AgC_4H(OC_6H_5)ClO_3$.	Found.
Silver	32.40	32.40

A solution of this salt, on standing, undergoes a decomposition similar to that taking place in a solution of the barium salt.

PHENOXYCHLORACRYLIC ACID.

The reaction taking place when mucophenoxychloric acid is decomposed by an excess of alkaline hydrate, is analogous to that occurring when mucophenoxybromic acid is treated in like manner, the products being formic and a substituted acrylic acid.* Phenoxychloracrylic acid is most advantageously prepared in the following manner. Potassic mucophenoxychlorate is added to an equal weight of potassic hydrate dissolved in twice its weight of water, the mixture being gently heated on the water bath. On cooling, potassic phenoxychloracrylate separates in well formed crystals; these are dissolved in water and the acid is precipitated from their filtered solution by the addition of hydrochloric acid. When recrystallized from hot water, and dried over sulphuric acid, it gave the following results: —

I. 0.1862 gram substance gave on combustion 0.3738 gram CO_2, and 0.0616 gram H_2O.
II. 0.2362 gram substance gave 0.1702 gram AgCl.
III. 0.2018 gram substance gave 0.1458 gram AgCl.

	Calculated for	Found.		
	$C_3H_2(OC_6H_5)ClCO_2$.	I.	II.	III.
Carbon	54.41	54.75		
Hydrogen	3.51	3.68		
Chlorine	17.92		17.84	17.89

The acid dissolves readily in alcohol, ether, benzol, ligroin, and carbon disulphide; is nearly insoluble in cold water, and only sparingly soluble in boiling water, from which it may be crystallized in long silky needles, melting at 104°–105°.

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* These Proceedings, Vol. XIX. p. 267.

Potassic Phenoxychloracrylate, $KC_3H(OC_6H_5)ClO_2$.

When a hot aqueous solution of phenoxychloracrylic acid is neutralized with potassic carbonate, and partially evaporated, potassic phenoxychloracrylate separates from the concentrated solution in well formed plates, which may be recrystallized from hot water, although quite soluble in the cold.

These crystals are permanent in the air, and lose no weight at 110°. The air-dried salt was analyzed with the following results: —

I. 0.3310 gram ignited with H_2SO_4 gave 0.1206 gram K_2SO_4.
II. 0.1929 gram ignited with H_2SO_4 gave 0.0707 gram K_2SO_4.

	Calculated for $KC_3H(OC_6H_5)ClO_2$.	Found. I.	Found. II.
Potassium	16.49	16.34	16.43

Calcic Phenoxychloracrylate, $Ca[C_3H(OC_6H_5)ClO_2]_2 . 5\,H_2O$.

A hot aqueous solution of the acid is neutralized with calcic carbonate and concentrated, when the calcium salt crystallizes out in clusters of long needles, which are permanent in the air. They lose most of their crystal water over sulphuric acid, and the whole at 110°.

I. 0.7847 gram air-dried salt lost at 110° 0.1343 gram H_2O.
II. 0.3240 gram air-dried salt, ignited with H_2SO_4, gave 0.0847 gram $CaSO_4$.

	Calculated for $Ca[C_3H(OC_6H_5)ClO_2]_2 . 5\,H_2O$.	Found. I.	Found. II.
Water	17.14	17.12	
Calcium	7.62		7.69

0.1684 gram salt, dried at 110°, gave, on ignition with H_2SO_4, 0.0525 gram $CaSO_4$.

	Calculated for $Ca[C_3H(OC_6H_5)ClO_2]_2$.	Found
Calcium	9.19	9.17

Baric Phenoxychloracrylate, $Ba[C_3H(OC_6H_5)ClO_2]_2 . 5\,H_2O$.

The hot aqueous solution of the acid is neutralized with baric carbonate, evaporated until a thin film appears on the surface, and then allowed to cool, when the barium salt separates in clusters of long silky needles. These crystals appear to be slightly efflorescent, losing on exposure to the air for several days less than a molecule of water.

I. 0.3640 gram salt dried between filter papers gave, on ignition with H_2SO_4, 0.1346 gram $BaSO_4$.

II. 0.7799 gram salt dried between filter papers lost, at 110°, 0.1140 gram H_2O.

	Calculated for	Found.	
	$Ba[C_3H(OC_6H_5)ClO_2]_2 . 5 H_2O$.	I.	II.
Water	14.47		14.60
Barium	21.52	21.64	

I. 0.1382 gram salt dried at 110° gave, on ignition with H_2SO_4, 0.6076 gram $BaSO_4$.

II. 0.1535 gram salt dried at 110° gave, on ignition with H_2SO_4, 0.6754 gram $BaSO_4$.

	Calculated for	Found.	
	$Ba[C_3H(OC_6H_5)ClO_2]_2$.	I.	II.
Barium	25.75	25.85	25.87

Argentic Phenoxychloracrylate, $AgC_3H(OC_6H_5)ClO_2$.

On adding argentic nitrate to a hot aqueous solution of ammonic phenoxychloracrylate, there is precipitated crystalline argentic phenoxychloracrylate, which may be recrystallized from hot water in beautiful feathery needles. Dried over sulphuric acid it gave the following results: —

I. 0.1759 gram salt gave 0.0821 gram AgCl.
II. 0.1165 gram salt gave 0.0547 gram AgCl.

	Calculated for	Found.	
	$AgC_3H(OC_6H_5)ClO_2$.	I.	II.
Silver	35.35	35.13	35.34

PHENOXYCHLORMALEIC ACID.

The structure of mucophenoxychloric acid has been further characterized by its oxidation to phenoxychlormaleic acid.

When a solution of mucophenoxychloric acid is heated with argentic oxide, there is deposition of metallic silver, and formation of argentic phenoxychlormaleate, which crystallizes from the hot filtered solution in minute stellate clusters. If the silver be precipitated with hydrochloric acid, and the filtered solution strongly concentrated, we obtain, on cooling, fine needles of phenoxychlormaleic acid. It has, however, been found advisable, on account of the sparing solubility of the silver salt, to prepare the acid in another way.

Hill and Cornelison found that mucophenoxybromic acid might advantageously be converted to phenoxybrommaleic acid by boiling the aqueous solution of its oxime;[*] and the same procedure has here been followed for the oxidation of mucophenoxychloric acid. Mucophenoxychloroxime is boiled with about twenty times its weight of water, until nothing separates on cooling. This solution is acidified with hydrochloric acid and extracted with ether, and the phenoxychlormaleic acid is removed from its ethereal solution by sodic carbonate, from which, in turn, it is separated by a second acidification and extraction; the ether is allowed to evaporate, and the crystalline residue is purified by sublimation in a current of carbonic dioxide. The anhydride thus obtained is dissolved in a small quantity of water, which, on spontaneous evaporation, deposits the acid as a mass of interlacing needles.

When thoroughly dried by pressure between filter papers, these crystals lose no weight in the air; but over sulphuric acid they suffer a gradual loss equivalent to one molecule of crystal water.

I. 0.2948 gram air-dried substance lost over H_2SO_4, 0.0195 gram H_2O.

II. 0.2769 gram air-dried substance gave on combustion 0.0860 gram H_2O and 0.4660 gram CO_2.

III. 0.1810 gram air-dried substance gave 0.0995 gram AgCl.

	Calculated for $C_4H_2(OC_6H_5)ClO_4 . H_2O$.	Found.		
		I.	II.	III.
Water	6.91	6.62		
Carbon	46.06		45.90	
Hydrogen	3.46		3.45	
Chlorine	13.62			13.60

0.1652 gram substance dried over H_2SO_4 gave 0.0960 gram AgCl.

	Calculated for $C_4H_2(OC_6H_5)ClO_4$.	Found.
Chlorine	14.64	14.38

The acid containing water of crystallization has no definite melting point, while that dried over sulphuric acid melts at 115°–122°, according to the mode of heating. It dissolves readily in water, alcohol, ether, chloroform, and benzol, is somewhat less soluble in ligroin, and only sparingly in carbonic disulphide. From hot benzol or ligroin it crystallizes in minute needles.

The identity of acids prepared by the two methods already described has been determined, in the absence of a definite melting point, by the identity of their anhydrides.

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[*] These Proceedings, *ante*, p. 53.

Phenoxychlormaleïc Anhydride, $C_4(OC_6H_5)ClO_3$.

This substance, purified by sublimation, was analyzed with the following results: —

I. 0.2000 gram substance gave 0.0441 gram H_2O, and 0.3929 gram CO_2.

II. 0.1054 gram substance gave 0.0664 gram AgCl.

	Calculated for $C_4(OC_6H_5)ClO_3$.	Found.	
		I.	II.
Carbon	53.45	53.56	
Hydrogen	2.23	2.45	
Chlorine	15.81		15.60

It melts sharply at 97°, sublimes in thin curving plates, and dissolves readily in water, alcohol, ether, chloroform, and benzol, but only sparingly in ligroin and carbonic disulphide.

Baric Phenoxychlormaleate, $BaC_4(OC_6H_5)ClO_4 . 4H_2O$.

This salt is most advantageously obtained in the following manner. Baric hydrate is added to a solution of the acid ammonium salt, prepared by boiling a solution of mucophenoxychloroxime, until the reaction is faintly alkaline. Baric bromide is then added in sufficient quantity to replace all the ammonium by barium, and on the addition of alcohol the new salt is precipitated in nodular aggregations of needles. It is filtered off, pressed dry, and redissolved in water, from which it is redeposited, on spontaneous evaporation, in bundles of long silky needles. When dried for analysis by pressure between filter papers, its weight remains constant in the air; but over sulphuric acid it suffers a loss corresponding to more than three molecules of crystal water, and at 110° there is a further loss, equivalent to the remainder of a fourth molecule.

I. 0.6161 gram air-dried salt lost over H_2SO_4, 0.0871 gram, and in addition at 110°, 0.0090 gram H_2O.

II. 0.1830 gram air-dried salt gave 0.0960 gram $BaSO_4$.

III. 0.1918 gram air-dried salt gave 0.1004 gram $BaSO_4$.

	Calculated for $BaC_4(OC_6H_5)ClO_4 . 4H_2O$.	Found		
		I.	II.	III.
Water	16.02	15.60		
Barium	30.50		30.84	30.77

0.2060 gram salt, dry at 110°, gave 0.1273 gram $BaSO_4$.

	Calculated for $BaC_4(OC_6H_5)ClO_4$.	Found.
Barium	36.29	36.33

Argentic Phenoxychlormaleate, $Ag_2C_4(OC_6H_5)ClO_4$.

This salt was prepared by precipitating a solution of the acid with argentic nitrate, as well as by heating a solution of mucophenoxychloric acid with argentic oxide.

In both cases it crystallized in clusters of colorless and somewhat opaque dendritic needles, which were only sparingly soluble in hot water, and even less so in cold.

0.3590 gram air-dried salt gave 0.2252 gram AgCl.

	Calculated for $Ag_2C_4(OC_6H_5)ClO_4$.	Found.
Silver	47.29	47.22